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Fire-retardant Polyester Composites from Recycled Polyethylene Terephthalate (PET) Wastes Reinforced with Coconut Fibre

(Komposit Poliester Perencat Api Berasaskan Bahan Buangan PET Kitar Semula Diperkuat Serabut Kelapa)

NURUL MUNIRAH ABDULLAH & ISHAK AHMAD*

ABSTRACT

Coconut fibre reinforced composite was prepared by blending unsaturated polyester resin (UPR) from waste PET with 0.3 v% of coconut fibre. The coconut fibres were pre-treated with sodium hydroxide followed by silane prior to inclusion into the UPR. The untreated coconut fibres reinforced composite were used as a control. Dricon® as a phosphate type of flame retardant was then added to the composite to reduce the flammability of the composite. The amount of Dricon® was varied from 0 to 10 wt% of the overall mass of resin. The burning properties and limiting oxygen index (LOI) of the treated and untreated composites increased with the addition of Dricon®. The tensile strength and modulus of both composites were also increased with the addition of Dricon®. The treated fibre composite with 5 wt% Dricon® showed the highest burning time and LOI with the values of 101.5 s and 34 s, respectively. The optimum tensile strength and modulus for treated fibre composite was at 5 wt% Dricon® whereas the untreated fibre composite was at 2.5 wt% loading of Dricon®. Thermogravimetry (TGA) analysis indicated that the degradation temperature increased with the addition of Dricon® up to 5 wt% into UPR/coconut fibre composites. Morphological observations indicated better distribution of Dricon® for treated fibre composite resulted in enhancement of the tensile properties of the treated fibre composite.

Keywords: Coconut fiber; flame retardant; polyester; polyethylene terephthalate

ABSTRAK

Komposit diperkuat serabut kelapa disediakan dengan mengadunkan resin poliester tak tepu (UPR) daripada bahan buangan PET pada komposisi 0.3% isi padu serabut kelapa. Pra-rawatan serabut kelapa telah dilakukan menggunakan natrium hidroksida diikuti oleh silana sebelum dicampurkan ke dalam UPR. Komposit diperkuat serabut kelapa tanpa rawatan telah digunakan sebagai kawalan. Dricon® iaitu sejenis perencat api fosfat kemudiannya ditambah kepada komposit untuk mengurangkan kebolehbakaran komposit. Komposisi Dricon® telah divariasi antara 0-10% berat jisim keseluruhan resin. Sifat pembakaran dan indeks pengehadan oksigen (LOI) bagi komposit terawat dan tanpa rawatan didapati telah meningkat dengan penambahan Dricon®. Kekuatan regangan dan modulus kedua-dua komposit juga telah meningkat dengan penambahan Dricon®. Komposit yang diperkuat serabut terawat dengan 5% berat Dricon® menunjukkan masa pembakaran dan LOI yang tertinggi dengan nilai 101.5 s dan 34 s masing-masing. Kekuatan regangan dan modulus yang optimum bagi komposit dengan serabut terawat adalah pada 5% berat Dricon® manakala komposit dengan serabut tidak terawat adalah pada 2.5% berat Dricon®. Analisis termogravimetri (TGA) menunjukkan bahawa suhu degradasi meningkat dengan penambahan Dricon® sehingga 5% berat yang ditambah ke dalam komposit UPR/serabut kelapa. Pemerhatian morfologi menunjukkan penyebaran Dricon® yang lebih baik bagi komposit dengan serabut yang dirawat menyebabkan peningkatan sifat regangan komposit.

Kata kunci: Kerintangan api; poliester; polietilena tereftalat; serabut kelapa

INTRODUCTION

Composite based on thermoset resin like unsaturated polyesters resin (UPR) is common for industrial applications including in aerospace, automotive or transportation and marine (Farias et al. 2009). The UPR are highly in demand because of their low cost, easy processing, low densities, good corrosion resistance and high strength to weight ratios (Atta et al. 2007). Recently, many researches have been carried out to use UPR composite from recycled polyethylene terephthalate (PET) due to environment concern (Ahmad et al. 2008, Tan et al. 2011). However, this type of composite is prone to fire damage especially when using natural fibre as the reinforcement and is essential to find adding materials that are not easily ignited and have a low total emission of heat when exposed to an ignition source (Shih et al. 2004). Therefore, unsaturated polyester composite reinforced natural fibre requires flame retardants to meet the fire protection standards.

Since natural fibre/polymer composites are increasingly used, the development of safe and environmental friendly flame retarded polymer composites is very important. Many studies on using flame retardant material in composite based natural fibre have been conducted. The effect of magnesium hydroxide and zinc borate as flame

retardants in mechanical properties and flammability of sisal/polylropylene (PP) composites has been studied by Suppakarn and Jarukumjorn (2009). They showed that adding flame retardant into sisal/PP composites reduced burning rate and increased thermal stability of the composites. Good distribution of flame retardant and sisal fibre in PP matrix was also observed.

In addition to reviewing the addition of flame retardant material in natural fibre/polymer composites, there is also research done by treatment of natural fibres with fire retardant materials. Suardana et al. (2011) reported that treated fibre with diammonium phosphate (DAP) had improved the flame resistance of bio-composites. Bio-composites with DAP-treated fibres also showed greater flexural modulus than untreated fibres. The best linear burning rate and weight loss rate were observed for fibre treatments with 5% DAP. Although a small number of studies have been carried out to utilize flame retardant in commercial polyester composite, no fire retardant material has been produced based on polyester composite synthesized from recycled PET. Therefore, the objective of the research was to produce fire retardant materials based on UPR from recycled PET.

In this research, the effect of Dricon® loading on the burning, mechanical and thermal properties of the coconut fibre (CF)-based UPR was carried out in determining its capability as a fire-retardant composite. The UPR was prepared by recycle the waste of poly(ethylene terephthalate) (PET). Varying amount of Dricon® was added in treated and untreated CF composites and comparison between the two composites were carried out.

Experimental Details

MATERIALS

Drinking PET bottles collected from garbage collector were washed, cut and grounded into fine pieces. Glycolysis of PET was done together with ethylene glycol and zinc acetate. Both chemicals were supplied by MERCK and Riedel-de Haën. Maleik anhydride, hydroquinone and styrene monomer from MERCK were used for the synthesis of unsaturated polyester resin. Curing process of UPR was done by using methyl ethyl ketone peroxide (MEKPO) as accelerator and cobalt aoctoate as an initiator, respectively, supplied by Revertex Sdn. Bhd. and Aldrich Co. The coconut fibres that act as a reinforcing agent were obtained from Fibromat (M) Sdn. Bhd. To modify the surface of CF by chemical treatment, sodium hydroxide (SYSTERM) and silane (Supplied by Dow Corning) were used. Dricon® flame retardant was obtained from Arch Wood Protection (M) Sdn. Bhd.

PREPARATION OF UNSATURATED POLYESTER RESIN

Fine pieces of PET were put into a four-necked flat bottom flask with the capacity of 1 L. Ethylene glycol was added into the flask at the ratio of PET:EG = 1:4 (w/w) together with 0.5% zinc acetate based on weight of PET as a catalyst. Then, magnetic stirrer was put into the flask to ensure the mixture occurred uniformly. This was carried out under reflux in nitrogen atmosphere with temperature at 190°C for 8 h by using heated silicon oil.

Unsaturated polyester resin (UPR) was prepared by using polyesterification reaction. Glycolysed product from glycolysis reaction was reacted with maleic anhydride at a fixed ratio of 1:1 for the hydroxyl to carboxyl groups. The polyesterification was carried out in a 1 L four-necked round bottom flask connected to a reflux condenser under nitrogen gas at 200°C. The experiment was done by heating the reactant in an oil bath. The acid value was monitored during the reaction and determined by the titration of 0.1 N NaOH into the weighed resin in 100 mL acetone according to ASTM D 1639-90 method. The reaction was stopped when the acid value reached 29-34 mg of KOH/g. The liquid resin was then cooled to 120°C and 0.45% hydroquinone based on weight PET was added to prevent the precuring of the resin. Finally, the liquid resin was dissolved in styrene monomer to achieve a 40% w/w styrene in the resin that equals to commercial UPR (Abu Bakar et al. 2006).

FIBRE TREATMENTS

CF in the form of unwoven mat was cut according to the size wanted. Before treatment was carried out, the fibre was first rinsed with distilled water to remove the dirt on the fibre surface. Washed CF was left to dry at room temperature and finally dried in oven for 2 h at 80°C.

CF surface was treated with 5% (w/v) sodium hydroxide followed by washing with distilled water for several times. Then, CF was dried at room temperature until the water was removed. After that, CF was dried in the oven at 80ºC and soaked in 0.5% silane solution for an hour and finally dried at room temperature (Cheng et al. 2010).

PREPARATION OF FIRE RETARDANT COMPOSITES

UPR reinforced CF composites incorporating Dricon® were prepared via *in situ* interactive polymerization. Predetermined weight fractions of Dricon® (0, 2.5, 5.0, 7.5 and 10.0 wt.%) were slowly added to the resin with vigorous mechanical stirring for 1 h at room temperature to afford homogeneity. The UPR/Dricon® mixture was then sonicated by an ultrasonicator for 15-20 min and continue stirring again before applying hand lay-up method. A stainless steel mould with the dimensions of 235 × 235 × 235 mm^3 and 3 mm of thickness was used. The curing of the UPR/Dricon® was done by the incorporation of 0.75 wt% cobalt octoate and 1.5 wt% methyl ethyl ketone peroxide (MEKPO) as an initiator and accelerator, respectively. The mixture was then poured on the mat form of treated and untreated CF. The volume fraction of CF in the composite, V_f, was approximately 0.3 with the thickness of specimens - 3 mm. The fire retardant composite was cured at room temperature for 24 h before removing it from the mould.

Finally, the composite was post cured in the oven at 60°C for 6 h.

ANALYSIS

The burning test was carried out to determine the fire resistivity of the treated and untreated CF composites according to the ASTM D 635-76. The flame retardant composites produced were cut to test samples with dimensional of 127 mm × 12.5 mm × 3 mm (length × width × thickness). The test samples were supported horizontally at one end as shown in Figure 1. The free end is exposed to a specified gas flame for 30 s. Time and extent of burning are measured and reported if the specimen does not burn. An average burning rate is reported for a material if it burns to the 100 mm mark from the ignited end. Limiting oxygen index (LOI) was conducted according to ASTM 2863 with Izod impact samples. Each specimen was clamped vertically in the centre of the column and was allowed to burn for the period of 3 min.

Thermogravimetry analysis (TGA) was carried out using a Mettler Toledo TGA/SDTA 518 thermogravimetry analyzer. The thermogravimetry curves were run from room temperature until 600°C under a nitrogen atmosphere flowing at 10 mL/min and at a scanning rate of 10°C/min.

Tensile test on fire retardant composites was determined according to ASTM D-638-91 standard. The measurements were done using Instron universal tensile machine (Model 5567) at a speed of 5 mm/min at room temperature.

The scanning electron micrograph of fracture surfaces following the tensile test of fire retardant composite materials was taken using scanning electron microscope (SEM), Philips XL30. The samples were first dried in oven to remove air moisture and then coated with a thin layer of gold by using sputter coater machine.

RESULTS AND DISCUSSION

BURNING TEST

Diagrams of test samples for treated and untreated CF composite after the burning test are shown in Figures 2 and 3 and the burning test results are shown in Figure 4. It can be clearly seen that burned areas for untreated CF composite at 0 wt% Dricon® is shorter than treated CF

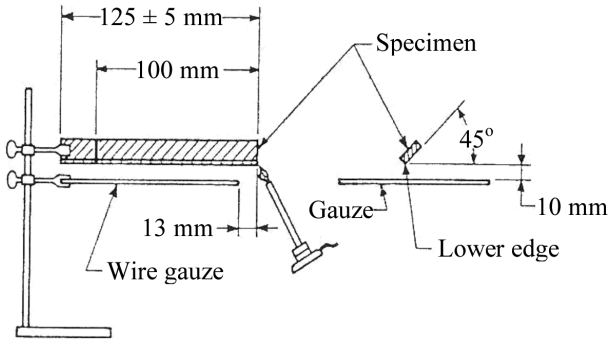

FIGURE 1. Schematic diagram for burning test set up

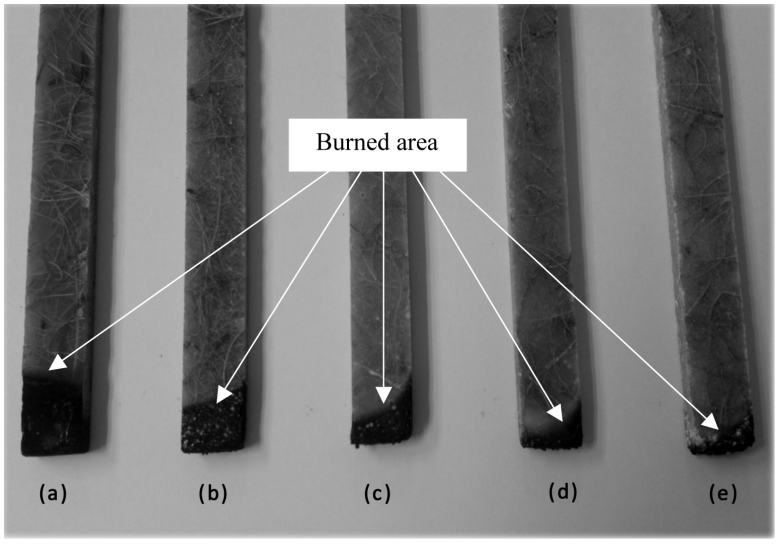

FIGURE 2. Photographs of untreated CF composite with (a) 0%, (b) 2.5%, (c) 5.0%, (d) 7.5% and (e) 10.0% Dricon® after burning test

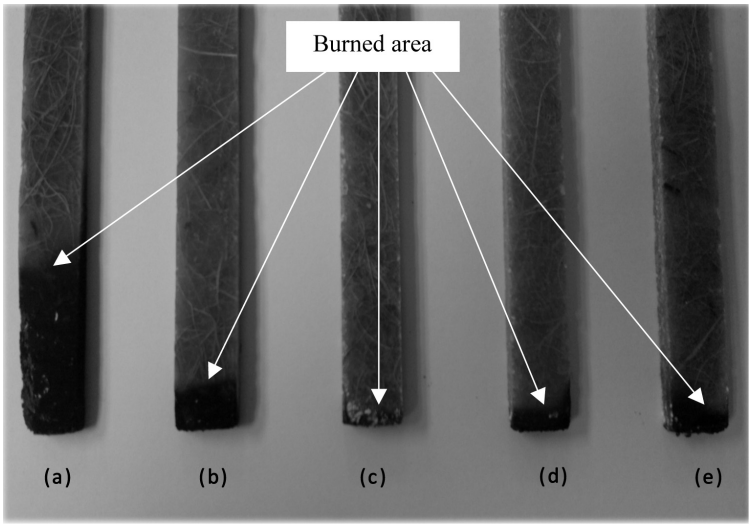

FIGURE 3. Photographs of treated CF composite with (a) 0%, (b) 2.5%, (c) 5.0%, (d) 7.5% and (e) 10.0% Dricon® after burning test

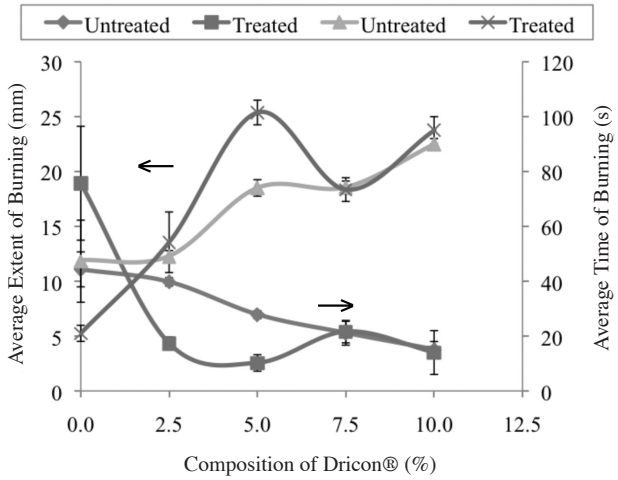

FIGURE 4. Burning test results for fire resistance of untreated and treated polyester CF composites

composite. This phenomenon can be related to the nature of natural fibre itself. As we know, CF is a natural fibre with high moisture content. Besides, untreated fibre is more hydrophilic than treated fibre. Polyester composite with untreated CF also showed longer average time of burning than treated CF composite at 0 wt% with the value are 43.7 and 21.0, respectively. While UPR matrix is hydrophobic and easier to burn due to its chemical structure that has high oxygen content. As a result, composite reinforced natural fibre that has a higher moister content and more hydrophilic can delay the burning process. Besides that, during the burning process, burned fibre is the initial source to the flame and molten polymer cannot flow away from the flame source. The polymer remains dispersed between the charred fibres which continue to maintain some structure while continuing to burn. It has been noted, that as a CF burned earlier, it is the initial source of fuel. Then UPR component will provides additional fuel to the gaseous phase at the high temperatures, produced by the combustion of the CF (Lewin 2005).

There are several ways to improve the fire and thermal properties of composites and one of that is by incorporation of inorganic fillers in polymer matrix. However, the enhancement of the mentioned properties strongly depends on the interaction between the filler and polymer. Therefore, homogeneous distribution of filler in polymer matrix and good interfacial adhesion are crucial for the performance of produced composites (Vargas et al. 2010). In this burning test, the optimum additions of Dricon® for untreated and treated CF composites are at 5 wt% and 10 wt% with the average time of burning are 101.5 s and 90.0 s, respectively. Previous research by Chong et al. (2012) had proved that treated fibre has better adhesion with the matrix compared with untreated fibre composite. Therefore, treated CF composite needs lower amount of Dricon® (5 wt%) to significantly improve the burning properties compared

with untreated CF composite (10 wt%). Similar results are also observed for LOI values as shown in Figure 5. The presence of a small amount of Dricon® for both untreated and treated CF composites increases considerably the LOI values of the polyester composite which indicates better fire retardant characteristics. Dricon® consists of three different substances of flame retardant which are boric acid, phosphoric acid and guanylurea phosphate. This flame retardant material occurred in the solid phase with each substance has its own mechanism. For example, acidic compounds lead to an increase in the degradation rate at lower temperature. Inorganic phosphate from guanylurea phosphate acts to abstract water mainly from cellulose which enables the formation of condensed unsaturated polymeric chains, while boron can form barriers on the composite to hinder oxygen access and encapsulate volatile substance (Roth et al. 2007).

MECHANICAL PROPERTIES

Figure 6 shows the tensile strength and modulus for treated and untreated CF composites with varying amount of Dricon®. It can be seen that the addition of Dricon® had increased the tensile strength and modulus for both composites. Both figures also show that treated CF composite has better mechanical properties than untreated CF composite. These results can be related to the better interfacial adhesion between treated fibre and matrix. During tensile test, the stress was transferred from the matrix to the fibre and Dricon® directly. When Dricon® was added into composite system that has better interfacial adhesion, the stress can be easily transferred leads to improve the mechanical properties.

For tensile strength, treated and untreated CF composites give the highest result at 5 wt% and 2.5 wt% of Dricon®, respectively. However, these results reduced

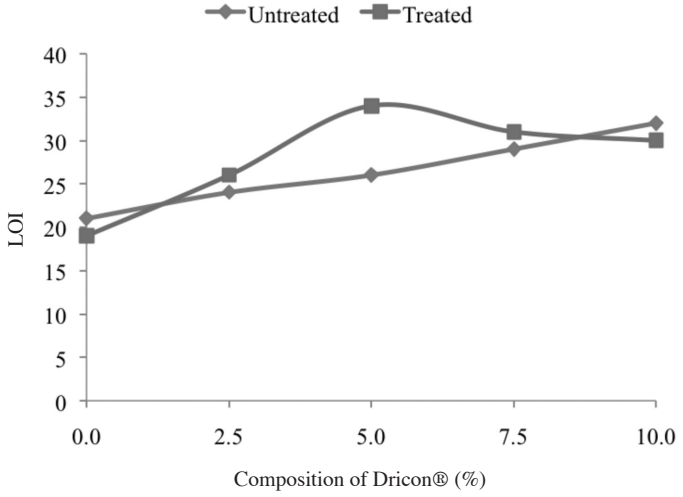

FIGURE 5. LOI of untreated and treated polyester-CF composites

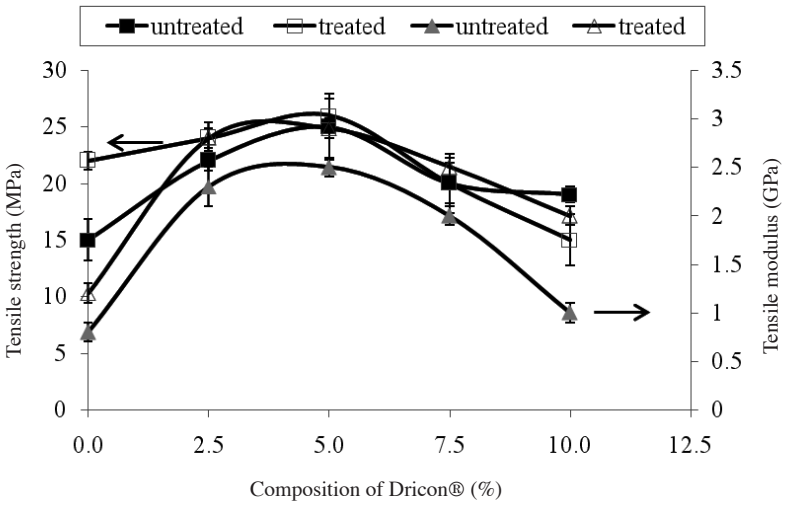

FIGURE 6. Effect of the composition of Dricon® on the tensile strength and tensile modulus for treated and untreated coconut fibre composites

with further addition of Dricon®. Addition of rigid particles such as Dricon® in the composite system leads to an increase in the brittleness. Furthermore, addition of too much of Dricon® can interrupt the composite system and creates the agglomeration of Dricon®. These made the stress not to disperse uniformly and resulted in reducing the mechanical properties (Dvir et al. 2003).

THERMOGRAVIMETRIC (TGA) ANALYSIS

TGA analysis is the most favoured technique for evaluating thermal stability of various polymers. Table 1 shows the TGA analysis for both treated and untreated composites at various Dricon® loadings. The thermal stability and residue of both composites increased with addition of Dricon®. Modesti et al. (2002) reported that addition of solid particles in the composites leads to higher thermal stability. When heat was introduced to the composites, Dricon® as rigid particles absorbed the same amount of heat and transferred it to the nearby Dricon® particles in the system. Therefore, when initial decomposition temperature of both composites increased, the thermal stability of those composites also increased. The highest initial decomposition temperature that could be achieved for both treated and untreated CF composites was at 5 wt% and 10 wt%, respectively.

Residual at 600°C referred to char yield of composites where high yield of residual char at high temperatures suggest that Dricon® is an efficient char agent. Besides, the resulting char also possesses good heat resistance at high temperatures (Chen et al. 2005).

MORPHOLOGICAL STUDY

SEM micrographs of treated CF and untreated CF composite at 5 wt% and 10 wt% Dricon®, respectively, have been examined to study the interaction and also the distribution of filler in the composite. The micrograph of the untreated CF composite (Figure 7) indicates that distribution of Dricon® was not uniform. Despite the highest value in fire resistance, but with too much of Dricon® has resulted in agglomeration of fillers which leads to reduce the mechanical properties. The SEM observations agree quite well with the reduction of tensile strength at 10 wt% Dricon®.

In contrast, different observation can be seen for treated CF composite with 5 wt% Dricon® as shown in Figure 8. Uniform dispersion of Dricon® indicates that the better interaction occurred between the Drion® and treated CF composite. Furthermore, it can be clearly seen that the Dricon® adhered well to the cell wall together with the CF. This also supports the result of tensile stress where the highest value is given at 5 wt% Dricon®.

Most of the researchers considered that layered flame retardant filler act through a physical rather than a chemical mechanism as they act in condensed phase behaving like inert filler and promoting the formation of protective barrier layers which shield the polymer matrix from the external thermal radiation and heat feedback from the flame (Yang et al. 2011). Therefore, morphological study on fire resistance of UPR/CF composites have demonstrated that addition of Dricon® only occurred at the surface of matrix and fibre and dispersed physically only.

CONCLUSION

The treated fibre composite showed better fire retarding, mechanical and thermal properties compared with the untreated fibre LOI value. However, untreated fibre composite indicated that at 10 wt% Dricon® showed better fire resistance. The loading of Dricon® is also able to improve mechanical and thermal properties of the composites and this indicated that the addition of Dricon® enhanced flame retardancy of coconut fibre/polyester composites without sacrificing their mechanical properties. From morphological examination, treated fibre composite revealed good distribution of Dricon® and was adhered well to cell wall together with the coconut fibre.

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TABLE 1. TGA analysis for untreated and treated composites at various loading of Dricon®

Addition of Dricon® (%)	Initial decomposition temperature (°C)		Residue at 600°C (%)	
	Untreated	Treated	Untreated	Treated
0	390.0	387.5	15	16
2.5	393.0	390.0	16	18
5	392.5	392.5	18	18
7.5	393.0	390.0	18	16
10	395.0	391.0	18	15

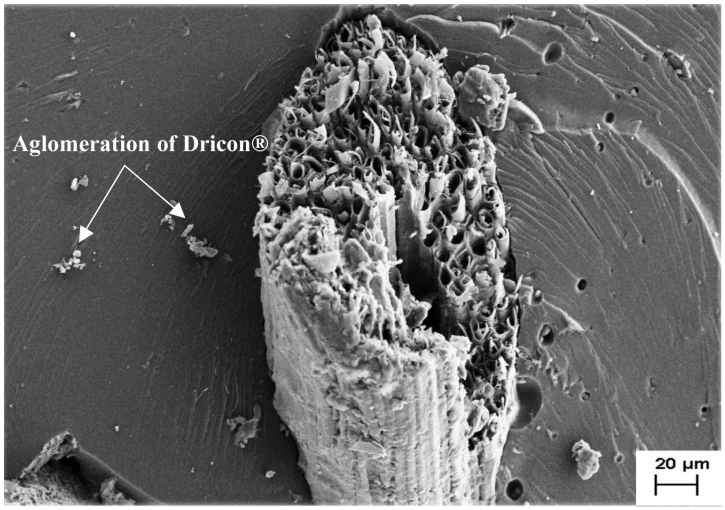

FIGURE 7. SEM micrograph for fire resistance of untreated CF composite

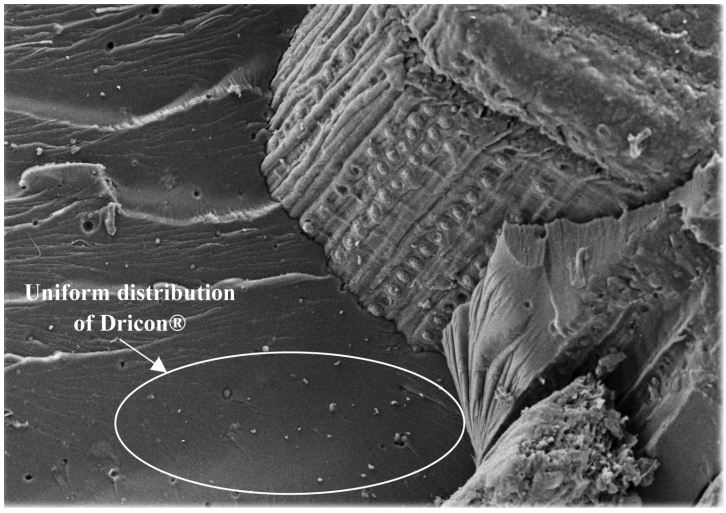

FIGURE 8. SEM micrograph for fire resistance of treated CF composite

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School of Chemical Sciences and Food Technology
Faculty of Science and Technology
Universiti Kebangsaan Malaysia
43600 Bangi, Selangor
Malaysia

*Corresponding author; email: gading@ukm.my

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